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THE COMPLEXITY OF THE CHEMICAL ELEMENTS¹

By Professor FREDERICK SODDY, M.A., F.R.S.

THE elements of the chemist are now known to be complex in three different senses. In the first sense the complexity is one that concerns the general nature of matter, and therefore of all the elements in common to greater or less degree. It follows from the relations between matter and electricity which have developed gradually during the past century as the result of experiments made and theories born within the four walls of this institution. Associated initially with the names of Davy and Faraday, they have only in these days come to full fruition as the result of the very brilliant elucidation of the real nature of electricity by your distinguished professor of physics, Sir Joseph Thomson. Such an advance, developing slowly and fitfully, with long intervals of apparent stagnation, needs to be reviewed from generation to generation, disentangled from the undergrowth that obscures it, and its clear conclusions driven home. This complexity of the chemical elements is a consequence of the condition that neither free electricity nor free matter can be studied alone, except in very special phenomena. Our experimental knowledge of matter in quantity is necessarily confined to the complex of matter and electricity which constitutes the material world. This applies even to the "free" elements of the chemist, which in reality are no more free than they are in their compounds. The difference is merely that, whereas in the latter the elements are combined with other elements, in the so-called free state they are combined with electricity. I shall touch but briefly on this first aspect, as in principle it is now fairly well understood. But its consistent and detailed application to the study of chemical character is still lacking.

The second sense in which the elements, or some of them at least, are known now to be complex has, in sharp contrast to the first, developed suddenly and startlingly from the recognition in radioactive changes, of different radio-elements, non-separable by chemical means, now called isotopes. The natural corollary of this is that the chemical element represents rather

¹ Lecture before the Royal Institution of Great Britain.

a type of element, the members of the type being only chemically alike. Alike they are in most of those properties which were studied prior to the last decade of last century and which are due, as we now think, to the outer shells of the atom, so alike that all the criteria, hitherto relied upon by the chemist as being the most infallible and searching, would declare them to be identical. The apparent identity goes even deeper into the region reached by X-ray spectrum analysis which fails to distinguish between them. The difference is found only in that innermost region of all, the nucleus of the atom, of which radioactive phenomena first made us aware.

But, though these phenomena pointed the way, and easily showed to be different what the chemist and spectroscopist would have decided to be identical, it did more. It showed that although the finer and newer criteria, relied upon by the chemist in his analysis of matter, must of necessity fail in these cases, being ultimately electrical in character, yet the difference should be obvious in that most studied and distinctive characteristic of all—the criterion by which Dalton first distinguished the different kinds of atoms—the atomic weight. Those who have devoted themselves to the exact determination of these weights have now confirmed the difference in two separate cases, which, in absence of what perhaps they might regard as “preconceived notions,” they were unable to discover for themselves. This is the experimental development to which I wish more especially to direct your attention. It indicates that the chemical analysis of matter is, even within its own province, superficial rather than ultimate, and that there are indefinitely more distinct elements than the ninety-two possible types of element accommodated by the present periodic system.

The third sense in which the elements are known to be complex is that which, in the form of philosophical speculations, has come down to us from the ancients, which inspired the labors of the alchemists of the Middle Ages, and which in the form of Prout's hypothesis has reappeared in scientific chemistry. It is the sense that denies to nature the right to be complex, and from the earliest times, faith outstripping knowledge, has underlain the belief that all the elements must be built up of the same primordial stuff. The facts of radioactive phenomena have shown that all the radio-elements are indeed made up of lead and helium, and this has definitely removed the question from the region of pure speculation. We know that helium is certainly a material constituent of the elements in the Proutian sense, and it would be harmless, if probably fruit-

less, to anticipate the day of fuller knowledge by atom building and unbuilding on paper. Apart altogether from this, however, the existence of isotopes, the generalization concerning the Periodic Law that has arisen from the study of radioactive change on the one hand and the spectra of X-rays on the other, and experiments on the scattering of α -particles by matter, do give us for the first time a definite conception as to what constitutes the difference between one element and another. We can say how gold would result from lead or mercury, even though the control of the processes necessary to effect the change still eludes us. The nuclear atom proposed by Sir Ernest Rutherford, even though, admittedly, it is only a general and incomplete beginning to a complete theory of atomic structure, enormously simplifies the correlation of a large number of diverse facts. This and what survives of the old electronic theory of matter, in so far as it attempted to explain the periodic law, will therefore be briefly referred to in conclusion.

THE FREE ELEMENT A COMPOUND OF MATTER AND ELECTRICITY

Although Davy and Faraday were the contemporaries of Dalton, it must be remembered that it took chemists fifty years to put the atomic theory on a definite and unassailable basis, so that neither of these investigators had the benefit of the very clear view we hold to-day. Davy was the originator of the first electrochemical theory of chemical combination, and Faraday's dictum, "the forces of chemical affinity and electricity are one and the same," it is safe to say, inspires all the modern attempts to reduce chemical character to a science in the sense of something that can be measured quantitatively, as well as expressed qualitatively. Faraday's work on the laws of electrolysis and the discovery that followed from it, when the atomic theory came to be fully developed, that all monovalent atoms or radicles carry the same charge, that divalent atoms carry twice this charge and so on, can be regarded to-day as a simple extension of the law of multiple proportions from compounds between matter and matter to compounds between matter and electricity. Long before the electric charge had been isolated, or the properties of electricity divorced from matter discovered, the same law of multiple proportions which led, without any possibility of escape, to an atomic theory of matter, led, as Helmholtz pointed out in his well-known Faraday lecture to the Chemical Society in this theater in 1881, to an atomic theory of electricity.

The work of Hittorf on the migration of ions, the bold and

upsetting conclusion of Arrhenius that in solution many of the compounds hitherto regarded as most stable exist dissociated into ions, the realization that most of the reactions that take place instantaneously, and are utilized for the identification of elements in chemical analysis, are reactions of ions rather than of the element in question, made very familiar to chemists the enormous difference between the properties of the elements in the charged and in the electrically neutral state.

More slowly appreciated, and not yet perhaps sufficiently emphasized, was the unparalleled intensity of these charges in comparison with anything that electrical science can show, which can be expressed tritely by the statement that the charge on a milligram of hydrogen ions would raise the potential of the world 100,000 volts. Or, if we consider another aspect, and calculate how many free hydrogen ions you could force into a bottle without bursting it, provided, of course, that you could do so without discharging the ions, you would find that, were the bottle of the strongest steel, the breech of a gun, for example, it would burst, by reason of the mutual repulsion of the charges, before as much was put in as would, in the form of hydrogen gas, show the spectrum of the element in a vacuum tube.

Then came the fundamental advances in our knowledge of the nature of electricity, its isolation as the electron, or atom of negative electricity, the great extension of the conception of ions to explain the conduction of electricity through gases, the theoretical reasoning, due in part to Heaviside, that the electron must possess inertia inversely proportional to the diameter of the sphere on which it is concentrated by reason of the electromagnetic principles discovered by Faraday, leading to the all-embracing monism that all mass may be of electro-magnetic origin.

This put the coping-stone to the conclusion that the elements as we apprehend them in ordinary matter are always compounds. In the "free" state they are compounds of the element in multiple atomic proportions with the electron. The ions, which are the real chemically uncombined atoms of matter, can no more exist free in quantity than can the electrons.

The compound may be individual as between the atom and the electron, or it may be statistical, affecting the total number merely of the opposite charges, and the element presumably will be an insulator or conductor of electricity accordingly. Analogously, with compounds, the former condition applies to unionized compounds such as are met with in the domain of

organic chemistry, or ionized, as in the important classes of inorganic compounds, the acids, bases and salts. Just as the chemist has long regarded the union of hydrogen and chlorine as preceded by the decomposition of the hydrogen and chlorine molecule, so he should now further regard the union itself as a decomposition of the hydrogen atom into the positive ion and the negative electron, and a combination of the latter with the chlorine atom.

One of the barriers to the proper understanding and quantitative development of chemical character from this basis is, perhaps, the conventional idea derived from electrostatics, that opposite electric charges neutralize one another. In atomic electricity or chemistry, though the equality of the opposite charges is a necessary condition for existence, there is no such thing as neutralization, or the electrically neutral state. Every atom being the seat of distinct opposite charges, intensely localized, the state of electric neutrality can apply only to a remote point outside it, remote in comparison with its own diameter. We are getting back to the conception of Berzelius, with some possibility of understanding it, that the atom of hydrogen, for example, may be strongly electro-positive, and that of chlorine strongly electro-negative, with regard to one another, and yet each may be electrically neutral in the molar sense. Some day it may be possible to map the electric field surrounding each of the ninety-two possible types of atom, over distances comparable with the atomic diameter. Then the study of chemical character would become a science in Kelvin's sense, of something that could be reduced to a number. But the mathematical conceptions and methods of attack used in electrostatics for macroscopic distances are ill-suited for the purposes of chemistry, which will have to develop methods of its own.

We have to face an apparent paradox that the greater the affinity that binds together the material and electrical constituents of the atom, the less is its combining power in the chemical sense. In other words, the chemical affinity is in inverse ratio to the affinity of matter for electrons. The helium atoms offer a very simple and instructive case. Helium is non-valent and in the zero family, possessing absolutely no power of chemical combination that can be detected. Yet we know the atom possesses two electrons, for in radioactive change it is expelled without them as the α -particle. The discharge of electricity through it and positive-ray analysis show that the electrons, or certainly one of them, are detachable by electric

agencies, although not by chemical agencies. One would expect helium to act as a diad, forming helides analogous to oxides.

Professor Armstrong for long advocated the view that these inert gases really are endowed with such strong chemical affinities that they are compounds that have never been decomposed. They certainly have such strong affinities for electrons that the atom, the complex of the $+$ ion and electrons, can not be decomposed chemically. Yet, in this case, where the affinity of the matter for the electron is at a maximum, the chemical combining power is absent.

These gases seem to furnish the nearest standard we have to electric neutrality in the atomic sense. The negative charge of the electrons exactly satisfies the positive charge of the matter, and the atomic complex is chemically, because electrically, neutral. In the case of the electro-positive elements, hydrogen and the alkali-metals, one electron more than satisfies the positive charge on the ion, and so long as the equality of opposite charges is not altered, the electron tries to get away. In the case of the electro-negative elements, such as the halogens, the negative charge, though equal presumably to the positive, is not sufficient to neutralize the atom. Hence these groups show strong mutual affinity, one having more and the other less negative electricity than would make the system atomically neutral like helium. The electron explains well the merely numerical aspect of valency. But chemical combining power itself seems to require the idea that equal and opposite charges in the atomic sense are only exactly equivalent in the case of the inert gases. None of these ideas are now new, but their consistent application to the study of chemical compounds seems curiously to hang fire, as though something were still lacking.

It is so difficult for the chemist consistently to realize that chemical affinity is due to a dissociating as well as to a combining tendency and is a differential effect. There is only one affinity, probably, and it is the same as that between oppositely charged spheres. But, atomic charges being enormous and the distances over which they operate in chemical phenomena being minute, this affinity is colossal, even in comparison with chemical standards. What the chemist recognizes as affinity is due to relatively slight differences between the magnitude of the universal tendency of the electron to combine with matter in the case of the different atoms. Over all is the necessary condition that the opposite charges should be equivalent, but this

being satisfied, the individual atoms display the tendencies inherent in their structure, some to lose, others to gain electrons, in order, as we believe from Sir Joseph Thomson's teaching, to accommodate the number of electrons in the outermost ring to some definite number. Chemical affinity needs that some shall lose as well as others gain. Chemical union is always preceded by a dissociation. The tendency to combine, only, is specific to any particular atom, but the energy and driving power of combination is the universal attraction of the + for the — change, of matter for the electron.

THE ELECTRICAL THEORY OF MATTER

Another barrier that undoubtedly exists to the better appreciation of the modern point of view, even among those most willing to learn, is the confusion that exists between the earlier and the present attempt to explain the relation between matter and electricity. We know negative electricity apart from matter as the electron. We know positive electricity apart from the electron, the hydrogen ion and the radiant helium atom or α -particle of radioactive change for example, and it is matter in the free or electrically uncombined condition. Indeed, if you want to find matter free and uncombined, the simple elementary particle of matter in the sense of complexity being discussed, you will go, paradoxically, to what the chemist terms a compound rather than to that which he terms the free element. If this compound is ionized completely it constitutes the nearest approach to matter in the free state. Thus all acids owe their common acidic quality to really free hydrogen, the hydrogen ion, a particle more different from the hydrogen atom than the atom is from the hydrogen molecule.

Positive electricity is thus emphatically not the mere absence of electricity, and any electrical theory of matter purporting to explain matter in terms of electricity does so by the palpable sophistry of calling two fundamentally different things by the same name. The dualism remains whether you speak of matter and electricity, or of positive and negative electricity, and the chemist would do well to stick to his conception of matter, until the physicist has got a new name for positive electricity which will not confuse it with the only kind of electricity that can exist apart from matter.

On the other hand, the theory of the electro-magnetic origin of mass or inertia is a true monism. It tries to explain consistently two things—the inertia of the electron and the inertia of matter—by the same cause. The inertia of the

former being accounted for by the well-known electro-magnetic principles of Faraday, by the assumption that the charge on the electron is concentrated into a sphere of appropriate radius; the 2,000-fold greater inertia of the hydrogen ion, for example, can be accounted for by shrinking the sphere to one two-thousandth of the electronic radius.

But the electrical dualism remains completely unexplained. Call the electron *E* and the hydrogen ion *H*. The facts are that two *E*'s repel one another with the same force and according to the same law as two *H*'s repel each other, or as an *H* attracts an *E*. These very remarkable properties of *H* and *E* are not explained by the explanation of the inertia. Are *E* and *H* made up of the same stuff or of two different stuffs? We do not know, and certainly have no good reason to assume, that matter minus its electrons is made of the same thing as the electron. We have still to reckon with two different things.

THE CHEMICAL ELEMENTS NOT NECESSARILY HOMOGENEOUS

I pass now to the second and most novel sense in which the elements, or some of them at least, are complex. In their discovery of new radioactive elements, M. and Mme. Curie used radioactivity as a method of chemical analysis precisely as Bunsen and Kirchoff, and later Sir William Crookes, used spectrum analysis to discover caesium and rubidium, and thallium. The new method yielded at once, from uranium minerals, three new radio-elements, radium, polonium and actinium. According to the theory of Sir Ernest Rutherford and myself, these elements are intermediate members in a long sequence of changes of the parent element uranium. In a mineral the various members of the series must coexist in equilibrium, provided none succeed in escaping from the mineral, in quantities inversely proportional to their respective rates of change, or directly proportional to their periods of average life. Radium changes sufficiently slowly to accumulate in small but considerable quantity in a uranium mineral, and so it was shown to be a new member of the alkaline-earth family of elements, with atomic weight 226.0, occupying a vacant place in the periodic table. Polonium changes 4,500 times more rapidly, and can only exist to the extent of a few hundredths of a milligram in a ton of uranium mineral. Actinium also, though its life period is still unknown, and very possibly is quite long, is scarce for another reason, that it is not in the main line of disintegration, but in a branch series which claims only a few per cent. of the uranium atoms disintegrating. In spite of this,

polonium and actinium have just as much right to be considered new elements, probably, as radium has. Polonium has great resemblance in chemical character both to bismuth and tellurium, but was separated from the first by Mme. Curie and from the second by Marckwald. In the position it occupies as the last member of the sulphur group, bismuth and tellurium are its neighbors in the periodic table. Actinium resembles the rare-earth elements, and most closely lanthanum, but an enrichment of the proportion of actinium from lanthanum has been effected by Giesel. The smallness of the quantities alone prevents their complete separation in the form of pure compounds as was done for radium.

The three gaseous members, the emanations of radium, actinium and thorium, were put in their proper place in the periodic table almost as soon as radium was, for, being chemically inert gases, their characterization was simple. They are the last members of the argon family, and the fact that there are three of about the same atomic weight was probably the first indication, although not clearly appreciated, that more than one chemical element could occupy the same place in the periodic table.

The extension of the three disintegration series proceeded apace; new members were being continually added, but no other new radio-elements—new, that is, in possessing a new chemical character—were discovered. The four longest-lived to be added, radio-lead or radium-D, as it is now more precisely termed, and ionium in the uranium series, and mesothorium-I and radiothorium in the thorium series, could not be separated from other constituents always present in the minerals, radium-D from lead, ionium and radiothorium from thorium, and mesothorium-I from radium. An appreciable proportion of the radioactivity of a uranium mineral is due to radium-D and its products, and its separation would have been a valuable technical achievement, but, though many attempts have been made, this has never been accomplished, and, we know now, probably never will be.

Seven years ago it was the general opinion in the then comparatively undeveloped knowledge of the chemistry of the radio-elements, that there was nothing especially remarkable in this. The chemist is familiar with many pairs or groups of elements, the separation of which is laborious and difficult, and the radiochemist had not then fully appreciated the power of radioactive analysis in detecting a very slight change in the proportions of two elements, one or both of which were radioactive. The case

is not at all like that of the rare-earth group of elements, for example, in which the equivalent or atomic weight is used as a guide to the progress of the separation. Here the total difference in the equivalent of the completely separated elements is only a very small percentage of the equivalent, and the separation must already have proceeded a long way before it can be ascertained.

Human nature plays its part in scientific advances, and the chemist is human like the rest. My own views on the matter developed with some speed when, in 1910, I came across a new case of this phenomenon. Trying to find out the chemical character of mesothorium-I, which had been kept secret for technical reasons, I found it to have precisely the same chemical character as radium, a discovery which was made in the same year by Marckwald, and actually first published by him. I delayed my publication some months to complete a very careful fractional crystallization of the barium-radium-mesothorium-I chloride separated from thorianite. Although a great number of fractionations were performed, and the radium was enriched, with regard to the barium, several hundred times, the ratio between the radium and mesothorium-I was, within the very small margin of error possible in careful radioactive measurements, not affected by the process. I felt justified in concluding from this case, and its analogy with the several other similar cases then known, that radium and mesothorium-I were non-separable by chemical processes, and had a chemical character not merely like, but identical. It followed that some of the common elements might similarly be mixtures of chemically identical elements. In the cases cited, the non-separable pairs differ in atomic weight from 2 to 4 units. Hence the lack of any regular numerical relationships between the atomic weights would on this view follow naturally.² This idea was elaborated in the Chemical Society's Annual Report on Radioactivity for 1910, in the concluding section summing up the position at that time. This was, I think, the beginning of the conception of different elements identical chemically, which later came to be termed "isotopes," though it is sometimes attributed to K. Fajans, whose valuable contributions to radioactivity had not at that date commenced, and whose first contribution to this subject did not appear till 1913.

In the six or seven years that have elapsed the view has received complete vindication. Really, three distinct lines of advance converged to a common conclusion, and, so far as is

² Trans. Chem. Soc., 1911, XCIX., 72.

possible, these may be disentangled. First, there has been the exact chemical characterization from the new point of view of every one of the members of the three disintegration series, with lives over one minute. Secondly, came the sweeping generalizations in the interpretation of the periodic law. Lastly, there has been the first beginnings of our experimental knowledge of atomic structure, which got beyond the electronic constituents and at the material atom itself.

In pursuance of the first, Alexander Fleck, at my request, commenced a careful systematic study of the chemical character of all the radio-elements known of which our knowledge was lacking or imperfect, to see which were and which were not separable from known chemical elements. Seldom can the results of so much long and laborious chemical work be expressed in so few words. Every one, that it was possible to examine, was found to be chemically identical either with some common element or with another of the new radio-elements. Of the more important characterizations, mesothorium-II was found to be non-separable from actinium, radium-A from polonium, the three B-members and radium-D from lead, the three C-members and radium-E from bismuth, actinium-D and thorium-D from thallium. These results naturally took some time to complete, and became known fairly widely to others working in the subject before they were published, through A. S. Russell, an old student, who was then carrying on his investigations in radioactivity in Manchester. Their interpretation constitutes the second line of advance.

Before that is considered, it may first be said that every case of chemical non-separability put forward has stood the test of time, and all the many skilled workers who have pitted their chemical skill against Nature in this quest have merely confirmed it. The evidence at the present day is too numerous and detailed to recount. It comes from sources, such as in the technical extraction of mesothorium from monazite, where one process is repeated a nearly endless number of times; from trials of a very great variety of methods, as, for example, in the investigations on radium-D and lead by Paneth and von Hevesy; it is drawn from totally new methods, as in the beautiful proof by the same authors of the electro-chemical identity of these two isotopes; it is at the basis of the use of radioactive elements as indicators for studying the properties of a common element, isotopic with it, at concentrations too feeble to be otherwise dealt with, and from large numbers of isolated observations, as well as prolonged systematic researches. One

of the finest examples of the latter kind of work, the Austrian researches on ionium, will be dealt with later. The most recent, which appeared last month, is by T. W. Richards and N. F. Hall, who subjected lead from Australian carnotite, containing therefore radium-D, to over a thousand fractional crystallizations in the form of chloride, without appreciably altering the atomic weight or the β -activity. So that it may be safely stated that no one who has ever really tested this conclusion now doubts it, and after all they alone have a right to an opinion.

This statement of the non-separability by chemical methods of pairs or groups of elements suffers perhaps from being in a negative form. It looks too much like a mere negative result, a failure, but in reality it is one of the most sweeping positive generalizations that could be made. Ionium we say is non-separable from thorium, but every chemist knows thorium is readily separated from every other known element. Hence, one now knows every detail of the chemistry of the vast majority of these new radio-elements by proxy, even when their life is to be measured in minutes or seconds, as completely as if they were obtainable, like thorium is, by the ton. The difference it makes can only be appreciated by those who have lived through earlier days, when, in some cases, dealing with the separation of radio-constituents from complex minerals, after every chemical separation one took the separated parts to the electroscope to find out where the desired constituent was.

As the evidence accumulated that we had to deal here with something new and fundamental, the question naturally arose whether the spectrum of isotopes would be the same. The spectrum is known, like the chemical character, to be an electronic rather than mass phenomenon, and it was to be expected that the identity should extend to the spectrum. The question has been tested very thoroughly by A. S. Russell and R. Rossi in this country, and by the Austrian workers at the Radium Institut of Vienna, for ionium and thorium, and by various workers for the various isotopes of lead. No certain difference has been found, and it may be concluded that the spectra of isotopes are identical. This identity probably extends to the X-ray spectra, Rutherford and Andrada having shown that the spectrum of the γ -rays of radium-B is identical with the X-ray spectrum of its isotope, lead.

(To be continued)